Research Article

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Synthesis and Characterization of Pure and Zn Doped HAp Nanoparticles by Microwave Irradiation Method

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ABSTRACT

Nanotechnology is an emerging concept in the field of science and technology. Hydroxyapatite (HAp) is a nano biomaterial incorporate as bone and teeth implants in the human body. The present work deals with the synthesis and characterization of pure and zinc doped HAp nanoparticles prepared by using the chemical co-precipitation method associated with the microwave irradiation process. The HAp was prepared using calcium hydroxide as a calcium source and orthophosphoric acid as the phosphorous source. The prepared sample was characterized by XRD, SEM, EDAX and UV analysis. The X-ray Diffraction (XRD) pattern reveals the crystalline size of the nanoparticles, Size and morphology of samples were examined by Scanning Electron Microscopy (SEM), and Energy Dispersion X-ray Diffraction (EDAX) analysis was used to investigate the purity and elemental composition of the sample. Then the optical properties and bandgap energy were carried out using Ultra-Violet spectroscopy (UV) and PL analysis.

Keywords: Co-preciptation method; Morphology; Optical Properties; Pure Hydroxyapatite; Zinc doped Hydroxyapatite.

1. INTRODUCTION

Nanotechnology is defined as a structure between 1-100 nanometer in size. While this is the most common definition of nanotechnology, researchers with various focuses have slightly different definitions. These possibilities may well be focused on the fate of free nanoparticles generated in nanotechnology processes and either intentionally or unintentionally released into the environment or actually delivered directly to individuals through the functioning of a nanotechnology-based product. Of special concern would be those individuals whose workplaces them in regular and sustained contact with free nanoparticles. Acetate**s** are salts or esters derived from acetic acid composed of two carbon atoms ionically bound to three hydrogen and two oxygen atoms (Symbol: CH_3COO) for a total formula weight of 59.05. Phosphoric acid, which is also a mineral acid, is represented by the formula H_3PO_4, and it contains one atom of phosphorus, four atoms of oxygen and three atoms of hydrogen. Calcium hydroxide, commonly referred to as slaked lime, is described by the chemical formula $Ca(OH)_2$. It is an inorganic compound that has a white, powdery appearance in its solid state. However, $Ca(OH)_2$ has a colourless appearance in its crystalline form.

2. MATERIALS & METHODS

2.1 Preparation of pure HAp nanoparticles

Hydroxyapatite (HAp) was synthesized by the chemical precipitation method. 3.7g of calcium hydroxide was dissolved with 50ml of distilled water, and 2.9g of orthophosphoric acid dissolved with 50ml of distilled water. Since both solution was stirred for 30 minutes. Then the orthophosphoric acid was added dropwise into the calcium hydroxide solution. The mixture was stirred 30 minutes. Then NaOH solution was added dropwise to maintain the pH level as 12. This was continuously stirred for half hours. The mixture was allowed to settle, then the precipitate was washed with double distilled water, and finally, it was kept in a microwave oven at 75w for 20 minutes. Then it was kept in a muffle furnace for 4 hours. The dried sample was grained in a mortar to get white colour pure Hydroxyapatite Nanoparticles.

2.2 Preparation of zinc doped hap nanoparticles

The pure HAp nanoparticles were prepared by taken 0.4 g of calcium hydroxide and 3g of orthophosphoric acid in separate beakers. Both solutions were dissolved in 50ml of distilled water, and it allowed to stirrer 30 minutes. After the orthophosphoric solution was added into the calcium hydroxide solution, followed to stirrer 30 minutes. The 2g of zinc acetate dihydrate dissolved in 50ml of distilled water it allowed and stirred for 30 minutes. Then the solution of zinc acetate dihydrate was added into the above mixture. It allowed to stirrer 30 minutes. NaOH was added dropwise into the solution to maintain the pH of 12 and it continuously stirred for 30 minutes. The precipitate was dried in a microwave oven at 75 watts for 30 minutes. Then the dried powder was grained by mortar followed to keep in

a muffle furnace 400 ºC for one hour, and then we get fine zinc doped Hydroxyapatite nanoparticles.

3. CHARACTERIZATION TECHNIQUES

3.1 XRD-Analysis

X-ray diffraction (XRD) relies on the dual wave/particle nature of X-rays to obtain information about the structure of crystalline materials. The lattice parameter of the sample was calculated using the following equation:

$$1/d^2 = (4(h^2+hk+k^2)/3a) + (1^2/c^2))$$

Where d is the spacing between the planes, a and c are the lattice parameter. The unit cell volume (V) of the sample was described using the given equation:

$$V = (\sqrt{3}/2) + a^2 + c^2$$

The average crystalline size of the sample was determined by using Scherer's formula.

$$D = K\lambda/\beta\cos\theta$$

Where D denotes the average crystalline size of the sample, K represents the broadening constant, denotes the wavelength of CuKα radiation source ($1.54A^0$), represents full width at half maximum, and an angle of diffraction is denoted by θ.

3.2 SEM and EDAX

The surface morphologies of synthesized Cu HAp samples were analysed using Scanning Electron Microscopic analysis (SEM). Energy dispersive spectroscopy is used to identify the elemental composition of the sample.

3.3 UV and PL

The emission of light or luminescence through this process is photoluminescence, PL. The absorption of light or luminescence through this process is UV-Visible Spectroscopy.

4. RESULT & DISCUSSION

4.1 XRD analysis

The XRD analysis is used to determine the crystalline size and phase identification of the prepared nanoparticles. The crystalline size of the particle was defined from Debye - scherrer's formula D=Kλ/β cos θ. Where λ- wavelength of XRD, β- full width half maximum, θ- Bragg's angle.

The lattice parameter calculated using the formula,1/d2= (4(h2+hk+k2)/3a2)+(l2/c2)). Where d is the plane spacing, a and c are the lattice parameters, which confirms the hexagonal structure. The unit cell volume (V) of the sample was described using the given equation,

$$V = (\sqrt{3}/2) + a2 + c2$$

The XRD pattern of prepared pure HAp and Zn doped HAp were shown in Fig. 1. The prepared sample confirms the presence of hexagonal structure and is well-matched with JCPDS file No: 09-0432. The broad diffraction peaks of the prepared HAp and Zn doped HAp at 2θ=42.130, 54.370 and 75.490 are clearly deducted. The indexed hkl planes are (302), (104) and (602). No impurity peaks were detected. The average crystalline size (D) of HAp and Zn doped HAp was 20.04 and 16.71nm. Thus the average crystalline size of Zn doped HAp small compared with HAp due to the reason of presence of polyphenols in the doped sample. The unit cell volume (V), lattice parameters a and c decreased due to an increase in crystalline size and were shown in table 1.

4.2 SEM analysis

The morphology of the synthesized nanoparticles was determined by scanning electron microscopy (SEM). The pure hydroxyapatite nanoparticles were exhibits cluster with agglomerated shape with a range of 51 to 71 nanometer (nm). Then the Zn doped Hap nanoparticles have the cluster morphology in the range of 43 to 72 nanometer(nm) Fig 2.

4.3 EDAX analyses

Energy-dispersive X-ray spectroscopy (EDX) provides a quantitative analysis. The purity and elemental composition of the sample were detected by this technique. From EDAX analysis, the existence of elements (calcium), P(), O(Oxygen), Na(sodium) confirmed the pure Hap nanoparticles. Then Zn doped Hap was identified from the elements of Zn (Zinc), Ca (calcium), P(),O (Oxygen) were shown in fig. 3.

4.4 FTIR analyses

The FTIR spectra predict the functional groups present in the sample. The FTIR spectrum of pure HAp shows the vibration modes of phosphate at 870.70cm-^{1}, 570.82cm-^{1} and 1044.26cm-^{1}. Hydroxyl groups for pure HAp is revealed at 3454.85 cm-^{1} and 3744.12 cm-^{1} .The vibration modes at 569.86cm-^{1}, 872.631cm-^{1} and 1043.31cm-^{1} reveal the presence of phosphate group and Hydroxyl groups at 3456.78 cm-^{1} and 3636.12 cm-^{1} for Zn-doped HAp.The peaks at 1421.28 cm-^{1}and 1420.32cm-^{1} represent the CH_3 stretching of carboxylic acid. The present groups were shown in table 3 and Fig 4.

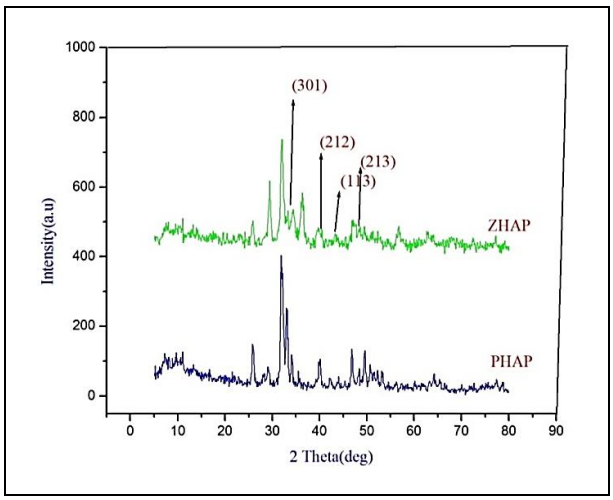

Fig. 1: XRD-analyses of pure and Zn doped HAp nanoparticles

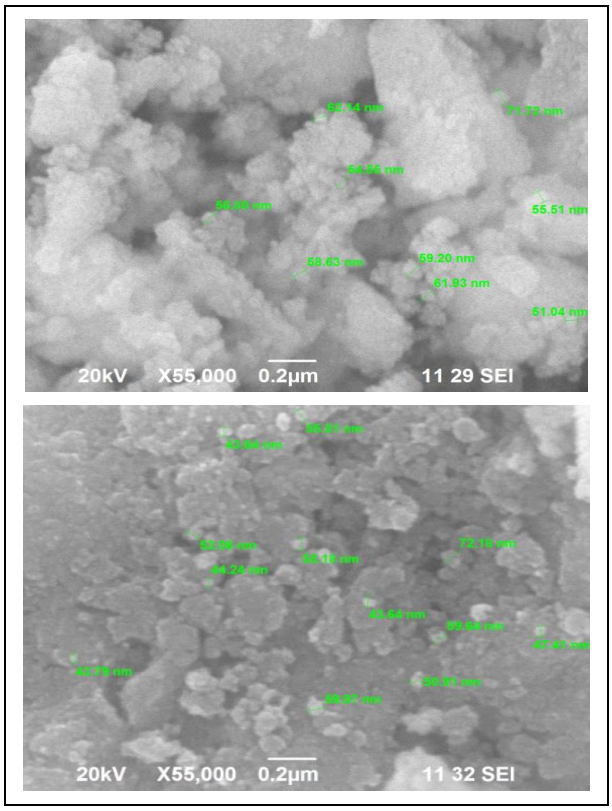

Fig. 2: SEM analysis of pure and Zn doped HAp nanoparticles

4.5 UV and PL analysis

UV –vis spectroscopy investigates the optical properties and bandgap energy of the sample. The absorption spectra of pure and Zn doped HAp nanoparticles are found in the wavelength of 348nm. The bandgap energy of both samples is similar in nature due to the quantum size effect and electronic structure modification. Table 4 shows the bandgap and absorption wavelength of the sample. Then fig 4.5shows the spectrum of pure and Zn doped HAp.

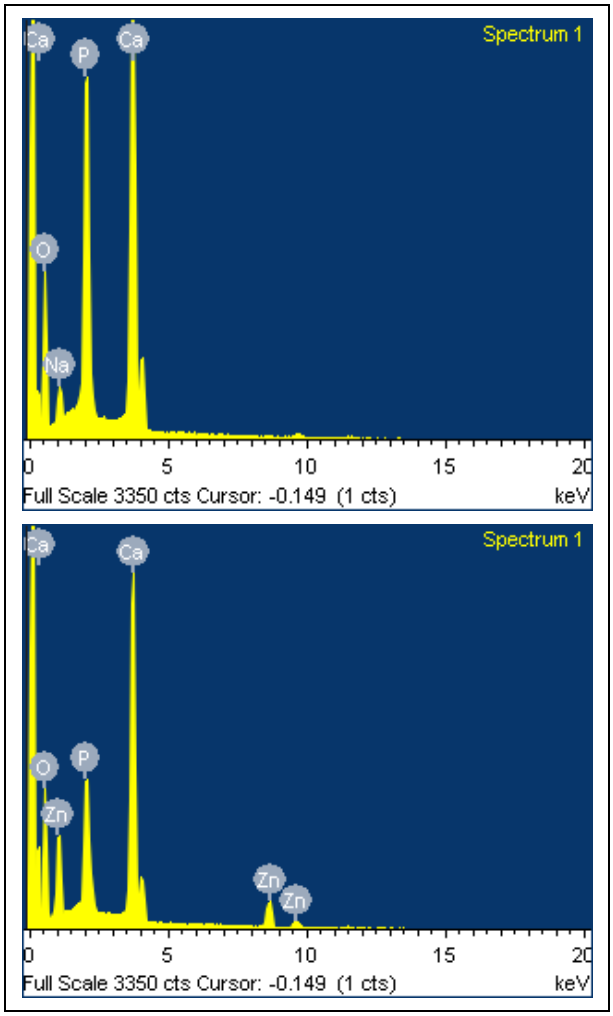

Fig. 3: EDAX analysis of pure HAP and Zn doped HAp nanoparticles

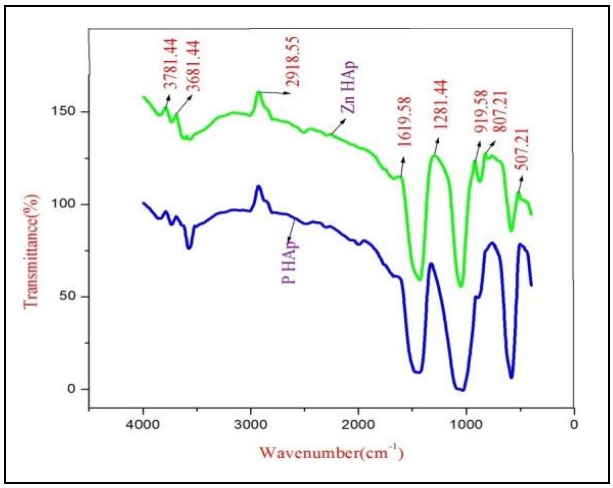

Fig. 4: FTIR analyses of pure and Zn doped HAp nanoparticles

Table 1. XRD-analyses of pure and ZnO doped HAp nanoparticles

Sample No	2θ (deg)	Crystalline size (nm)	Average crystalline size	hkl	Lattice constant		Unit cell volume
					a = b	c	
HAP	39.10	21.1135	19.1441	212	9.5492	6.8938	532.84
	43.22	19.7615		113			524.98
	49.50	16.5575		213			526.50
Zn-HAP	39.60	9.7443	14.2583	212	9.4033	6.8966	510.94
	43.35	13.1534		113			591.91
	49.40	19.8773		213			531.72

Table 2. EDAX Analysis of pure HAP and Zn doped HAp nanoparticles

Sample	Element	Weight %	Atomic Wt%
HAP	OK	51.23	70.08
	NaK	2.93	2.79
	PK	13.05	9.22
	CaK	32.79	17.91
Zn-HAP	OK	52.76	74.84
	PK	6.89	5.05
	CaK	27.86	15.78
	ZnK	12.49	4.34

Table 3. FTIR analyses of pure HAp and Zn doped HAp nanoparticles

S.No	Sample Name	WAVE NUMBER (cm^{-1})				
		O-H stretching vibration	C-H stretching vibration	C=C stretching vibration	CH_3 stretching vibration	P-O stretching vibration
1.	HAp	3766.76	2918.88	1673.03	1320.47	797.04
2.	Zn-HAp	3781.44	2918.55	1619.58	1281.44	807.21

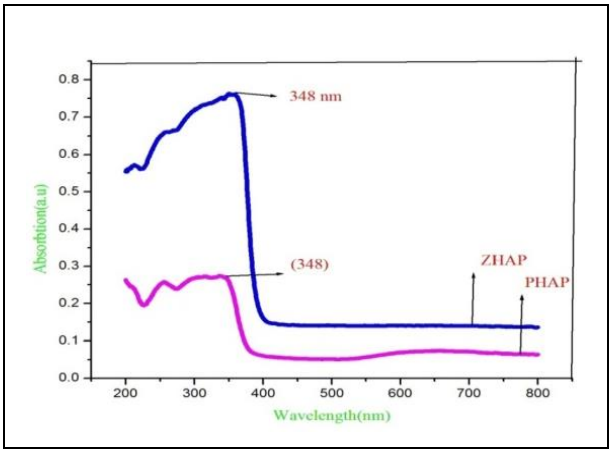

Fig. 5: UV-analysis of HAp and Zn doped HAp nanoparticles

Table 4. Wavelength and bandgap energy of HAp and Zn doped Hap

S.No	Sample name	Wavelength (nm)	Bandgap energy (eV)
1	HAp	348	3.56
2	Zn-HAp	348	3.56

4.6 Photo Luminance Spectroscopy

The intensity of emission radiations was absorbed by photoluminescence spectroscopy. The emission radiation of HAp and Zn-HAp are shown in Fig 6.6. The excitation wavelength that occurs at the ranges for both samples is 383 nm. The standard bandgap energy

of HAp around in the range, while the calculated bandgap energy of the samples is shown in fig: 6.

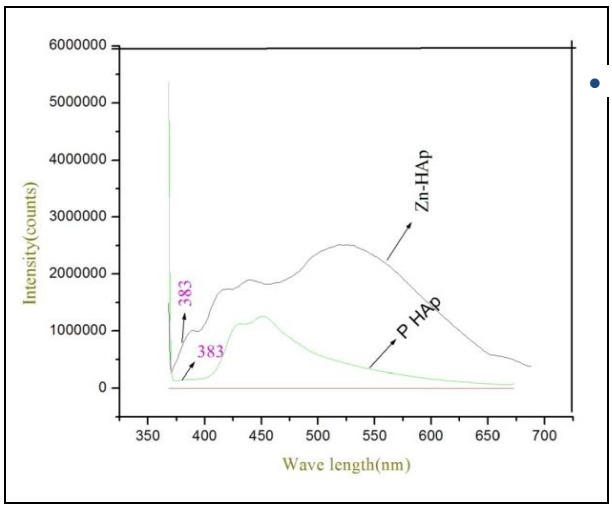

Fig. 6: PL analysis of pure and Zn doped HAp nanoparticles

5. CONCLUSION

The present work deals with the synthesis of pure and Zn doped Hydroxyapatite nanoparticles using the microwave irradiation method. The XRD pattern confirmed the crystalline size of the sample. The average crystalline size (D) of HAp and Zn doped HAp was 20.04 and 16.71nm. The crystalline size decreases in Zn-HAp when compared with HAp. Then FTIR spectrum reveals the functional groups present in the sample. However, SEM predicts the spherical shaped morphological structure, and EDAX confirms the elemental composition of calcium and phosphate and zinc groups are present in the sample. The bandgap energy and optical absorption were determined from UV and PL analysis. The observed bandgap energy for both samples is 3.56 eV.

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